United States Patent Office

2,793,154

Patented May 21, 1957

2,793,154

PYRETHRUM PESTICIDE SYNERGIZED WITH LOWER ALKYL ARYL KETONE

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No Drawing. Application June 10, 1955, Serial No. 514,782

Claims priority, application Great Britain June 15, 1954

9 Claims. (Cl. 167—24)

This invention relates to improved pest combating compositions.

It is known to use compositions comprising pyrethrins for combating pests. Usually the pyrethrins are employed in the form of an extract of the active principle of a plant of the genus Pyrethrum and conveniently may be applied, as solutions in petroleum distillate fractions, in the form of liquid sprays.

While it is recognised that the pyrethrins have a degree of toxicity for many insect pests, they are of particular value in providing the means of rapidly immobilising the pests and it is common practice to include in the pyrethrin containing composition at least one other component which although slower acting is of higher toxicity. By the use of such compositions it is possible to ensure that the pests are rapidly immobilised until the slower acting component has had time to be effective. Thus, in the application of insecticidal containing sprays to the killing of house flies it is considered desirable to include in the composition a component such as pyrethrin which provides a high knock down rate.

Pyrethrins and extracts containing pyrethrins are expensive and it is therefore desirable to reduce as far as possible the quantities of these materials employed in the compositions.

It has been shown that the addition of certain compounds, which are not necessarily insecticidal, to these compositions leads to an increase in the efficiency of the compositions and thus, by their inclusion, permits a reduction in the amount of pyrethrins employed.

A compound, which in admixture with another component gives a composition having a toxicity greater than equivalent amounts of the compound or the component when used alone, is known as a synergist.

Examples of synergists which have been used in sprays for combating house-flies are iso-butyl undecylenamide and sesame oil. Among the compounds which have been tried and found to lack synergistic products is included chalcone (alpha-benzalacetophenone).

Usually the compositions containing pyrethrins are employed in the form of sprays and the technical literature contains a description of a wide variety of solvents which may be employed for producing a solution of suitable characteristics for application in this manner. Thus a number of compositions are described containing petroleum fractions together with an oxygenated solvent, such as ketones. Thus compositions have been described containing an extract of pyrethin in kerosene or a heavy petroleum oil together with a phenol and as solvent a cyclic ketone such as cyclohexanone.

It has now been found that in addition to their properties as solvents, aryl alkyl ketones have the unexpected property of acting as a synergist for pyrethrins.

It is an object of the present invention to provide improved pest-combating compositions. It is a further object to provide pest-combating compositions containing

pyrethrins in the presence of an economically attractive synergist therefor.

According to the present invention there is provided an improved pest combating composition comprising at least one pyrethrin and at least one aryl alkyl ketone.

Preferably the composition consists of a solution of pyrethrum extract and an aryl alkyl ketone in a hydrocarbon distillate fraction.

Suitably, the distillate fraction is a kerosene or white spirit fraction of petroleum.

Preferably the ketone is an aryl alkyl ketone in which the aryl group consists of an unsubstituted or alkyl substituted phenyl group.

Preferably, also, the ketone is an aryl alkyl ketone in which the alkyl group comprises 1–4 carbon atoms.

Particularly preferred ketones are acetophenone and the methyl acetophenones. Other ketones which may be employed include butyro phenone (propyl phenyl ketone) valero phenone (butyl phenyl ketone) and iso-capro phenone (iso amyl phenyl ketone).

In general it is found convenient to include in the pest combating compositions a proportion of a highly toxic insecticide to increase the percentage kill obtained by the insecticide. Suitable insecticides include the gamma isomer of benzene hexachloride, p,p' dichlorodiphenyl trichloroethane and dieldrin.

Preferably the insecticidal compositions according to this invention contain 0.02–0.075% wt./vol. of total pyrethrins.

Preferably the ratio of aryl alkyl ketone/total pyrethrins is not greater than 15/1 wt./wt. It is particularly preferred that the ratio lies in the range 5/1 to 15/1 wt./wt.

Preferably the insecticidal composition contains up to 0.5% wt./vol. of a highly toxic insecticide, for example, benzene hexachloride.

By the use of compositions according to the present invention it is possible to obtain a satisfactorily short insect knock-down time, while effecting an economy in the use of the relatively expensive pyrethrum extract.

The invention is illustrated but in no way limited by the following examples.

The kerosene employed in the examples was a premium grade commercial petroleum kerosene fraction having the following characteristics

Specific Gravity @ 60° F./60° F. A. S. T. M. Distillation (D.86/54)		0.7825
IBP	°C.	172
2% recovered @	°C.	180
5% recovered @	°C.	185
10% recovered @	°C.	190
20% recovered @	°C.	197
30% recovered @	°C.	203
40% recovered @	°C.	208.5
50% recovered @	°C.	214
60% recovered @	°C.	219
70% recovered @	°C.	225
80% recovered @	°C.	232
90% recovered @	°C.	244
FBP	°C.	268
Recovery	percent	98
Residue	do	1.3
Loss	do	0.7
Recovery @ 185°C	do	5
Recovery @ 200°C	do	25
Recovery @ 240°C	do	87.5

EXAMPLE 1

The essence of synergism is that Pyrethrum plus synergist has a greater toxicity than either material alone, the toxicity of the mixture being greater than the sum of its parts. It has been found that if the synergist is sprayed before the Pyrethrum, the synergistic effect is just as strong and this is used to distinguish true synergism from pseudo synergism such as that exhibited by lubricating oils and oleic acid which have the physical effect of stabilizing the droplet size. To establish the true synergistic action of acetophone, the following tests were made in triplicate.

(*a*) The flies were sprayed with 1 ml. of kerosene and left in contact with the spray for ten minutes. The killing chamber was then aired by use of the exhaust fan and the flies left for fifteen minutes before being sprayed with 1 ml. of 0.05% w./v. pyrethrins blend.

(*b*) The flies were sprayed with 1 ml. of a 0.5% w./v. blend of acetophenone in kerosene and left in contact with the spray for ten minutes. The killing chamber was then aired as previously and the flies given fifteen minutes to recover before being sprayed with 1 ml. of the 0.05% w./v. pyrethrins blend.

(*c*) The flies were sprayed with 1 ml. of kerosene and the same airing procedure adopted as in the tests under (*a*) and (*b*) before being sprayed with a blend of 0.05% w./v. pyrethrins plus 0.5% w./v. acetophenone.

The mean results of these three sets of tests are recorded in Table 1.

(*a*) the volume of the chamber was 18.7 cu. ft. (i. e. approx. 1/12 of the vol. of the standard Peet-Grady chamber).

(*b*) the dosage used was in all cases 1 ml. (i. e. 1/12 of the dosage employed in the standard method).

(*c*) a spraying pressure of 10 lb./sq. in. was employed employing as the spray gun "Aerograph Artists Brush" with a No. 2 nozzle.

(*d*) the number of test insects employed was 90–104 per test.

Table 2

Insecticide	0.1% w./v. Pyrethrins	0.05% w./v. Pyrethrins	0.05% w./v. Pyrethrins with Acetophenone percent w./v. as below						
			0.05% w./v.	0.15% w./v.	0.25% w./v.	0.40% w./v.	0.50% w./v.	0.60% w./v.	0.75% w./v.
Ratio $\frac{\text{Acetophenone}}{\text{Pyrethrins}}$ w./w			1/1	3/1	5/1	8/1	10/1	12/1	15/1
Time for 50% K. D. (seconds)	88	120	92	107	103	100	103	92	89
Time for 90% K. D. (seconds)	153	241	231	191	160	159	154	144	190
Time for 100% K. D. (seconds)	373	538	360	445	433	420	400	360	300
Percent K. D. in 600 seconds	100	100	100	100	100	100	100	100	100
Percent Kill in 24 hours	39.2	13.6	14.7	12.6	13.0	14.0	22.4	22.6	23.0

Table 1

Method of Spraying Insecticide	Method (*a*)	Method (*b*)	Method (*c*)
Time for 50% K. D. (Secs.)	120	77	89
Time for 90% K. D. (Secs.)	218	140	140
Time for 100% K. D. (Secs.)	360	367	570
Percent K. D. in 600 seconds	100	100	100
Percent Kill in 24 hours	19.3	22.3	21.8

EXAMPLE 2

Pyrethrum extract (containing 25% w./v. of total pyrethrins) and/or acetophenone were dissolved in kerosene.

The compositions were employed in a series of biological tests upon the common house fly (*Musca domestica L.*), based on the Peet-Grady test, with the results shown in the following Table 2. The Peet-Grady test is described in Soap and Sanitary Chemicals, 1954, Blue Book and Catalogue Edition, page 243 et seq.

The method therein described was modified in the following respects:

EXAMPLE 3

The experiment described in Example 2 was repeated carrying out three assays on each of three different generations of *Musca domestica L.* The mean results of the nine assays for each blend were as shown in Table 3.

Table 3

Insecticide	0.1% w./v. Pyrethrins	0.05% w./v. Pyrethrins	0.05% w./v. Pyrethrins with Acetophenone percent wt. as below									
			0.125	0.025	0.05	0.15	0.25	0.35	0.40	0.50	0.60	0.75	1.0
Ratio $\frac{\text{Acetophenone}}{\text{Pyrethrins}}$ w./w			0.25/1	0.5/1	1/1	3/1	5/1	7/1	8/1	10/1	12/1	15/1	20/1
Time for 50% K. D. (Secs.)	82	133	106	110	114	106	101	82	90	101	101	103	96
Time for 90% K. D. (Secs.)	149	276	259	275	253	268	179	174	177	178	173	201	230
Time for 100% K. D. (Secs.)	325	538	410	420	420	497	390	360	340	387	360	300	390
Percent K. D. in 600 seconds	100	100	100	100	100	100	100	100	100	100	100	100	100
Percent Kill in 24 hours	44.7	13.4	13.0	13.1	14.7	17.0	17.3	18.3	18.3	17.3	19.8	19.0	22.0

EXAMPLE 4

The effect of adding chlorinated hydrocarbon contact insecticides to a Pyrethrum spray synergised with acetophenone was studied by preparing, with kerosene as solvent, three blends

(*a*) containing 0.05% w./v. pyrethrins, 0.35% w./v. acetophone and 0.5% w./v. DDT (pp' dichlorodiphenyl trichloro ethane)

(*b*) containing 0.05% w./v. pyrethrins 0.35% w./v. acetophenone and 0.1% w./v. pure B. H. C. (pure gamma isomer of benzene hexachloride).

(*c*) containing 0.05% w./v. pyrethrins 0.35% w./v. acetophenone and 0.1% w./v. dieldrin (hexachloro-epoxy-octahydrodimethano naphthalene).

These blends were assayed in triplicate against a blend of 0.05% w./v. pyrethrins with 0.35% w./v. acetophenone using a 0.05% w./v. pyrethrins spray as control and the mean results of the tests are recorded in Table 4.

Table 4

Insecticide	0.05% w./v. Pyrethrins	0.05% w./v. Pyrethrins plus 0.35% w./v. acetophenone	0.05% w./v. Pyrethrins plus 0.35% Acetophenone with—		
			0.5% w./v. DDT	0.1% w./v. B.H.C.	0.1% w./v. Dieldrin
Time for 50% K. D. (Secs.)	138	85	79	78	99
Time for 90% K. D. (Secs.)	277	135	135	157	234
Time for 100% K. D. (Secs.)	4,455	260	358	570	570
Percent K. D. in 600 seconds	100	100	100	100	100
Percent Kill in 24 hours	16.7	19.5	100	100	100

EXAMPLE 5

p-Methylacetophenone, propio-phenone and benzophenone were tested for synergistic activity by preparing three blends containing 0.05% w./v. pyrethrins with 0.35% w./v. of the appropriate compound under test in kerosene and assaying in triplicate each blend against a 0.05% w./v. pyrethrins blend. The mean results are recorded in Table 5.

Table 5

Insecticide	0.05% w./v. Pyrethrins	0.05% w./v. Pyrethrins with 0.35% w./v.		
		p-Methyl-aceto-phenone	Propio-phenone	Benzo-phenone
Time for 50% K. D. (Secs.)	137	102	111	104
Time for 90% K. D. (Secs.)	256	241	363	390
Time for 100% K. D. (Secs.)	590	592	600	600
Percent K. D. in 600 seconds	100	100	100	100
Percent Kill in 24 hours	13.9	20.3	22.7	27.6

We claim:

1. A pest-combating liquid composition comprising pyrethrin and phenyl alkyl ketone in which the alkyl group comprises 1–4 carbon atoms, the ratio of the total weight of phenyl alkyl ketone to total weight of the pyrethrin being in the range of from about 5:1 to about 15:1, said pyrethrin and phenyl alkyl ketone being in solution with a liquid hydrocarbon distillate fraction derived from petroleum.

2. A composition as specified in claim 1 in which the fraction is a kerosene fraction of petroleum.

3. A composition as specified in claim 1 in which the fraction is a white spirit fraction of petroleum.

4. A composition as specified in claim 1 in which the ketone is acetophenone.

5. A composition as specified in claim 1, and having included therein, the gamma isomer of benzene hexachloride.

6. A composition as specified in claim 1, and having included therein, pp' dichlorodiphenyl trichloro ethane.

7. A composition as specified in claim 1, and having included therein, dieldrin.

8. A composition as specified in claim 1 in which the total amount of pyrethrins present is 0.02–0.075% wt./vol.

9. A pest-combating liquid composition comprising 0.02–0.075% wt./vol. of pyrethrin; acetophenone, the ratio of the weight of acetophenone to the total weight of pyrethrin lying in the range of from about 5:1 to about 15:1; a pesticide selected from the group consisting of the gamma isomer of benzene hexachloride, p,p'-dichlorodiphenyl trichloro-ethane, and dieldrin, the foregoing being in solution with a liquid hydrocarbon distillate fraction derived from petroleum.

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